

Fluorescence spectroscopy as a tool for quality assessment of humic substances

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Fluorescence spectroscopy belongs to modern, non-destructive, rapid and relatively cheap methods, as well as for many years it was successfully used in studies of organic compounds in the fields of medicine, biology and chemistry. On the other hand, soil organic matter is a group of compounds with a complex spatial structure showing a large number of groups with different kinds of fluorophores. This could suggest the possibility of application of fluorescence spectroscopy in assessing the quality of humic substances as well as in monitoring of their chemical transformations.

The aim of study was chemical description of humic and fulvic acids based on fluorescence spectra, as well as an attempt of evaluation of changes occurring under the influence of different pH and during interactions with various concentrations of metal.

The humic and fulvic acids were isolated from chemically different soils. The measurements were carried out on Hitachi fluorescence spectrometer in solutions with a concentration of humic acids 40mg dm⁻³, at pH from 3 to 7, and for the evaluation of the metal impact: with increasing Zn concentrations (0-50mg dm⁻³). The fluorescence spectra were recorded in the form of synchronous and emission-excitation matrices (EEM).

Studies have shown the presence of different groups of fluorophores. Synchronous spectra were characterized by a well-separated bands showing fluorescence in the area of low, medium and high wavelengths, suggesting the presence of structures, both weakly and strongly humified. EEM spectra revealed map of fluorophores within wide ranges of emission and excitation. Fluorophores differed in both position and intensity. The highest intensity was observed for compounds with the lowest humification degree which might be due to high amount of hydroxyl groups.

The pH increase caused in most cases increase in the fluorescence intensity of all the groups of fluorophores which could result from a larger spatial expansion of the molecule and its functional groups. The increase in pH also caused shift of fluorescence maxima towards longer wavelengths which could indicate an increase in the share of strongly humified groups.

Both the synchronous and eem spectra showed significant differences in the processes of interaction of humic substances with zinc ions. The metal induced fluorescence quenching, which was evidence on complexation process. Analysis of the data allowed in all cases, to evaluate the metal concentration at which saturation of an organic compound taken place, as well as estimate of the stability of complex compounds. Fluorescence technique demonstrated also differences between the studied humic substances. The changes related to the position of the fluorophores as well as to their intensity. Strongly humified structures, with higher molecular weight and greater degree of aromaticity showed activity at higher wavelengths, while "younger" structures - at lower wavelengths. Complexation of the metal could be also possible under consideration of the particular fluorescence areas.